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Using Sparingly Dissoluble Calcium Salts as Reactants

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Supersaturation Control in Aragonite Synthesis Using Sparingly Dissoluble Calcium Salts as Reactants

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Abstract

Sparingly dissoluble calcium salts were studied as reactants in the synthesis of needle-like precipitated calcium carbonate (PCC). Morphology and aspect ratio of the PCC particle were characterized with SEM. Polymorphs and crystal size were characterized using x-ray diffraction. The counter-ions of the sparingly dissoluble salts influenced growth kinetics of PCC as well as the polymorphs and morphology of product particles. Either chrysanthemum-like or needle-like aragonite can be synthesized from calcium sulfate and sodium carbonate depending on the supersaturation and synthesis conditions. Low concentration and slow addition rate of sodium carbonate solution were favorable to the formation of aragonite. Addition of sodium sulfate in the reaction system (calcium chloride and sodium carbonate) promoted the formation of aragonite due to the decrease of supersaturation; however, it decreased the crystal size of aragonite. The influence of pH of the reaction showed behavior similar to that given in references. An optimal temperature for the formation of aragonite was found to be about 60°C.

Key Words: Calcium carbonate, Aragonite, Morphology, Filler, PCC

1. Introduction

Inexpensive calcium carbonate has been widely applied as filler in paper, plastics, and rubber. It was thought that needle-like calcium carbonate filler might give excellent properties of paper for bulk, brightness, opacity, and strength, as well as improved retention [1-5]. Gill and Scott [6] found that PCC of the aragonite and scalenohedral forms was superior to the rhombohedral and ground carbonates in optical properties at high loadings. The relation between preparation conditions and morphology of calcium carbonate has been widely studied [7-9]. Generally, aragonite calcium carbonate is liable to give needle-like or spindle-like morphology [4,10,11].

Calcite is the thermodynamics-stable phase of calcium carbonate [12]. Kato et al. [13] found that agitating the reaction solution with a magnetic stirrer first yielded aragonite, which then transformed into calcite. Microwave heating resulted in the transformation of vaterite into calcite with a similar shape to that of vaterite. It was thought that recrystallization of vaterite into calcite had taken place without a change in its shape [14]. Therefore, controlled conditions have to be used in the synthesis of aragonite. Generally, a temperature above 60°C was favorable to the formation of aragonite [4,8]. Tai and Chen [10] found that aragonite prepared at room temperature generally was rosette or dumbbell in form. They found that pure aragonite usually was obtained at above 70°C. The one prepared at 58°C showed a needle-like shape, which was similar to the results of Xyla and Koutsoukos [15]. Kitano and Hood [16] thought that formation of vaterite was favored by the presence of impurities like Ba in a temperature of 40-70°C. pH of the reaction solution is very important for the formation of the desired phase. Chen et al. [8] found the favorable pH for the formation of calcite was ca. 8.6 at 30°C. High pH favored the formation of aragonite. Liu et al. [8] prepared needle-like aragonite at the condition of pH to approximately 9 and the temperature above 60°C. Tai and Chen found vaterite was the major product in the pH region of 8.5-10, a result similar to that reported by Kralij et al. [17]. Aragonite showed a maximum at pH 11, and calcite was dominant at higher pH than 12 [10]. In order to synthesize needle-like aragonite, both inorganic and organic additives have been studied. Among

inorganic additives much attention has been paid to magnesium-containing compounds [18-25]. A lot of chelating agents [3,19,20,26,27] were studied to improve the formation of aragonite.

It is well known that both nucleation and growth of crystalline depend on supersaturation of the solution. Therefore, supersaturation will affect both polymorphs and morphology of PCC. Needle-like aragonite has to be synthesized in a given supersaturation region. High supersaturation is favorable to the formation of calcite. Therefore, controlled solution concentration has to be used for synthesizing aragonite [4,5,10,19,28]. However, low concentration means low yield of industrial production.

In terms of NCF (Nurton, Cabrera, and Frank) model [29], growth rate of crystal can be calculated by:

$$R_G = A \sigma^2 \tanh(B / \sigma)$$

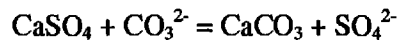
where A and B are constants that depend on temperature and step spacing. σ is relative supersaturation:

$$\sigma = \Omega^{1/2} - 1$$

Ω is saturation ratio:

$$\Omega = \alpha_{Ca^{2+}} \alpha_{CO_3^{2-}} / K_{SP}$$

K_{SP} is solubility product. $\alpha_{Ca^{2+}}$ and $\alpha_{CO_3^{2-}}$ are activities of ions [30]. Therefore, if a soluble salt is used as reactant the concentration has to be very low in order to synthesize aragonite. If a sparingly soluble salt suspension of the salt was used as a reactant in the synthesis, although the content of the total solid reactant in the suspension can be very high, the concentration or supersaturation of related ions is still very low. In terms of solubility product of $CaSO_4$ and $CaCO_3$ [31], the following reaction will take place:



The reactant constant is:

$$K = \frac{[SO_4^{2-}]}{[CO_3^{2-}]} = \frac{K_{SPCaSO_4}}{K_{SPCaCO_3}} = \frac{3.14 \times 10^{-5}}{3.36 \times 10^{-9}} = 9.35 \times 10^3$$

This suggests that (a) the conversion of $CaSO_4$ to $CaCO_3$ can be almost completed if enough CO_3^{2-} is added, and (b) the concentration of calcium in the solution can be much lower than when $Ca(OH)_2$ (or CaO) is used as a reactant. The Ca^{2+} concentration in $CaSO_4$ suspension, calculated from K_{sp} , is only half of that of $Ca(OH)_2$. (c) $[Ca^{2+}]$ in $CaSO_4$ suspension can be adjusted by $[SO_4^{2-}]$ independently on pH. In $Ca(OH)_2$ suspension, although low $[Ca^{2+}]$ can be obtained by increasing $[OH^-]$ or by high pH, too high pH is disadvantageous for the formation of aragonite. Therefore, the supersaturation of PCC synthesis can be reduced by the use of sparingly dissoluble calcium salt, which should be favorable for synthesizing needle-like aragonite. This research aims at synthesizing needle-like aragonite by supersaturation control using different sparingly soluble calcium salts as a start reactant, and the focus is on calcium sulfate. The main purpose of this research is to explore favorable conditions for aragonite formation and study the relation of polymorphs and preparation conditions.

2. Experimental Section

2.1 Synthesis of precipitated calcium carbonate

Following is a typical procedure for the synthesis of calcium carbonate, which was used in the investigation on the influence of sodium carbonate concentration. 0.03 mol calcium sulfate dehydrate (Mallinckrodt, reagent) was added to 50 mL of DI water and then was heated to 70°C. After agitation for 15 minutes 0.01 mol/L sodium carbonate (Aldrich, 99.5%) solution was added to the suspension at 8 mL/min. Finally, the product suspension was filtrated without aging, rinsed three times with 50 mL of DI water, and dried at 120°C for 2 h. Using the same procedure calcium carbonate was synthesized from calcium iodate (Aldrich, 98%), calcium fluoride (Aldrich, 99.9%), calcium hydroxide (Aldrich, 95%), and sodium carbonate where sodium

carbonate was 20% excessive. To study the effect of $[\text{SO}_4^{2-}]$, the sodium carbonate solution was dropped to a calcium sulfate suspension with a different concentration of sodium sulfate. In the study on the effect of the adding rate of sodium carbonate, similarly, 1.00mol/L sodium carbonate was added to a calcium sulfate suspension with 0.64mol/L sodium sulfate at different rate. In order to realize the effect of pH of the suspension on morphology and polymorphs of PCC, calcium sulfate was added to 50 mL of 0.1mol/L ammonium sulfate (Aldrich, reagent) solution. Then sodium hydroxide (Aldrich, 50% aqueous solution) solution was added to the suspension to different preset pH. A pH meter (Corning pH-30, Portugart) was used to measure pH value at a temperature lower than 50°C. At 70°C the pH was measured with pH test paper (DIP-STRIK 5-9, Micro Essential Laboratory).

2.2 Characterization

A scanning microscope (JEOL, JSM-35C, Tokyo, Japan) was used to visualize morphology of the calcium carbonate particle and to measure the aspect ratio of particles where an average value was obtained from more than 50 particles. A filament voltage of 15kV was used. An average aspect ratio was calculated.

XRD spectra of the product were measured with a PW1800 x-ray diffractometer (Philips, USA). A step size of 0.02° and scanning speed of 0.4 S per step were used to record spectra in the region from 20°-80° or 20°-32°. Crystal sizes of aragonite and calcite were measured with the x-ray broadening method [32,33]. Peak widths of $d_{(104)}=3.3035\text{\AA}$, $2\theta=29.404^\circ$ of calcite and $d_{(111)}=3.396\text{\AA}$, $2\theta=26.213^\circ$ of aragonite are used in the calculation. Single crystal silicon was used to calibrate broadening of the instrument. The polymorphic fraction of aragonite in crystalline calcium carbonate can be evaluated using the following equation [34] when no vaterite exists:

$$y = \frac{3.9S_a}{S_c + 3.9S_a}$$

where y is the calculated fraction of aragonite and S_c and S_a are the integrated intensities of x-ray diffraction spectra characteristic of calcite ($d_{(104)}=3.3035\text{\AA}$, $2\theta=29.404^\circ$) and aragonite ($d_{(111)}=3.396\text{\AA}$, $2\theta=26.213^\circ$), respectively.

3. Results and Discussion

3.1 Comparison of different sparingly soluble calcium salts as reactants

The basic goal of this research is to control supersaturation of reactant using a sparingly dissoluble calcium salt so that the formation of calcite can be restrained. The solubility of calcium carbonate and saturation solubility of related calcium salts are given in Table 1. Except for $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$, all the other four salts are lower than that of CaCO_3 , so thermodynamically $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$ can't be used as a starting reactant for PCC synthesis. XRD spectra of corresponding products prepared from these salts and sodium carbonate are given in Fig. 1. Both $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ gave calcite because of a high concentration (1.00 mol/L) of sodium carbonate used here. $\text{Ca}(\text{IO}_3)_2$ gave both calcite and vaterite, while $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{IO}_3)_2$ possess closed solubility. These results indicate that counter-ions of sparingly dissoluble calcium salt play an important role for the polymorphs of PCC. However, when CaF_2 was used, there were almost no diffraction peaks of CaCO_3 . A calculation in terms of reactant amount, concentration, and K_{sp} of CaF_2 and CaCO_3 indicates that CaCO_3 content in a solid product should be as high as 9.37 wt% if the reaction reached thermodynamic equilibrium. Theoretically, this amount of CaCO_3 should give marked XRD diffraction peaks. The fact that almost no calcium carbonate formed when CaF_2 was used as a reactant means that not only the thermodynamic equilibrium but also reaction kinetics play an important role in the synthesis of PCC from sparingly soluble salt.

Table 1. Solubility product and saturation solubility of different calcium salts [31]

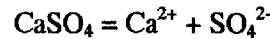
Salt	K_{sp}	Solubility (mol/L)
$\text{CaC}_2\text{O}_4\text{H}_2\text{O}$	2.32×10^{-9}	4.817×10^{-5}
CaCO_3 (Calcite)	3.36×10^{-9}	5.797×10^{-5}
CaF_2	3.45×10^{-11}	2.051×10^{-4}
$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	3.14×10^{-5}	5.604×10^{-3}
$\text{Ca}(\text{IO}_3)_2$	6.47×10^{-6}	1.053×10^{-2}
$\text{Ca}(\text{OH})_2$	5.02×10^{-6}	1.079×10^{-2}

3.2 Effect of sodium carbonate concentration/adding rate on morphology and polymorphs

Relative supersaturation of CaCO_3 in the synthesis can be calculated by [30]:

$$\sigma = \Omega^{1/2} - 1 = [\alpha_{\text{Ca}^{2+}} \alpha_{\text{CO}_3^{2-}} / K_{sp}]^{1/2} - 1$$

For a CaSO_4 suspension Ca^{2+} concentration, calculated from following reaction equilibrium to be 5.604×10^{-3} mol/L:



$$K_{sp} = 3.14 \times 10^{-5} = [\text{Ca}^{2+}] \times [\text{SO}_4^{2-}]$$

At the very beginning of the synthesis and ignoring the effect of ion strength, the relative supersaturation of the reaction can be written as:

$$\begin{aligned} \sigma &= [5.604 \times 10^{-3} [\text{CO}_3^{2-}] / 3.36 \times 10^{-9}]^{1/2} - 1 \\ &= 1.29 \times 10^3 [\text{CO}_3^{2-}]^{1/2} - 1 \end{aligned}$$

The solubility of CaSO_4 will slowly decrease with the reaction because of the production of SO_4^{2-} during the reaction. On the other hand, local supersaturation of the suspension depends directly

on the concentration of sodium carbonate. XRD spectra of calcium carbonate and fraction of aragonite prepared from different concentrations of sodium carbonate are given in Fig. 2 and Fig. 3, respectively. The fraction of aragonite increases with the decrease of sodium carbonate concentration, i.e., the decrease of the total supersaturation of the suspension. When the sodium carbonate concentration decreased to 0.025 mol/L, calcite in the product almost completely disappeared. The SEM images of these samples are given in Fig. 4a to 4c, respectively. A direct measurement of the needle size from these SEM photos, however, gives a much larger result than that of XRD broadening of (111) face, which gives a crystal size of less than 200 nm. This result suggests that these needle-like particles are polycrystalline. It is very interesting to note that the morphology of the final calcium carbonate changed from needle-like to chrysanthemum-like clusters when the sodium carbonate concentration was increased from 0.004 to 0.1 mol/L. At the sodium carbonate concentration of 0.004 mol/L, a needle-like PCC with an aspect ratio of 9.72 ± 0.44 was obtained.

The relation of aragonite fraction to adding rate is given in Fig. 5. With the decrease of adding rate, the aragonite fraction increases. When the adding rate of 1.00 mol/L sodium carbonate solution was 0.4 mL/min, almost 96% of the product was aragonite. Here the supersaturation of the reaction depended on both nucleation rate of PCC and feeding rate of reactants for a constant concentration. There is an induction period before the formation of PCC after the addition of sodium carbonate, especially when some organic inhibitor exists [35-37]. Therefore, a high adding rate of reactant means high supersaturation. The SEM image is given in Fig. 6 from an adding rate of 0.15 mL/min. Selected area diffraction on one of these particles was carried out with TEM. Some diffraction circles indicated that the particle is polycrystalline. This result means that the nucleation rate of aragonite is too high or the growth rate was too low so that small aragonite crystals appeared continuously with the addition of sodium carbonate solution. Then these small aragonite crystals aggregated into big particles. XRD broadening gives a crystal size less than 50 nm, which is much smaller than the results shown in Figure 2.

3.3 Effect of sodium sulfate concentration

Concentration of calcium ions in reaction suspension will decrease with the increase of sulfate ions concentration because of following equation:

$$[Ca^{2+}] = 3.14 \times 10^{-5} / [SO_4^{2-}]$$

Therefore, Ca^{2+} concentration and reactant supersaturation can be decreased by addition of sodium sulfate in the suspension. Aragonite fractions measured from XRD diffraction peak areas are given in Fig. 7, which show a tendency to increase with the increase of sulfate ion concentration. The crystal size is given in Fig. 8. No marked difference was found for calcite crystal size. Aragonite size, however, decreased with the increase of sulfate ion concentration. These results mean that the addition of sodium sulfate promoted the formation of aragonite due to the decrease of supersaturation. It should be noted that the counter-ions sulfate may also remarkably affect the nucleation and growth kinetics and fraction of aragonite.

3.4 Influence of suspension pH and temperature

The fraction of aragonite in the sum of aragonite and calcite prepared under different pH is given in Fig. 9. A maximum can be found at a pH of 10.5. This is close to the results of Tai and Chen [10], where a maximum was found at a pH of 11.

Temperature influences dissolution rate of calcium sulfate, nucleation, and growth rate of PCC and therefore the morphology. A favorable temperature for the formation of aragonite was thought to be above 60°C [4,8,10]. XRD characterization indicated that at 26°C and 35°C some vaterite appeared. This is in agreement with the result of Kitano and Hood [16]. The fraction of aragonite of the PCC prepared at different temperatures is given in Fig. 10. The maximum of aragonite appeared at 60°C. The change of the suspension pH with the temperature during the synthesis is given in Fig. 11. With the increase of the temperature, the pH of the reaction suspension decreased. The difference of pH might result from the dissolution and conversion of

solids in the solution at different reaction temperatures. These results also suggested that the dissolution kinetics of sparingly dissoluble salt also are very important for controlling PCC crystal structure and morphology.

4. Conclusion

Sparingly dissoluble calcium salts can be used as reactants in the synthesis of PCC. The counter-ions of the salt influenced the growth kinetics of PCC and the morphology of product particles. Chrysanthemum-like or needle-like aragonite can be synthesized from calcium sulfate and sodium carbonate. Low concentration and low adding rate of sodium carbonate solution were favorable to the formation of aragonite. Addition of sodium sulfate promoted the formation of aragonite due to the decrease of supersaturation. An optimal temperature for the formation of aragonite was found to be ca. 60°C.

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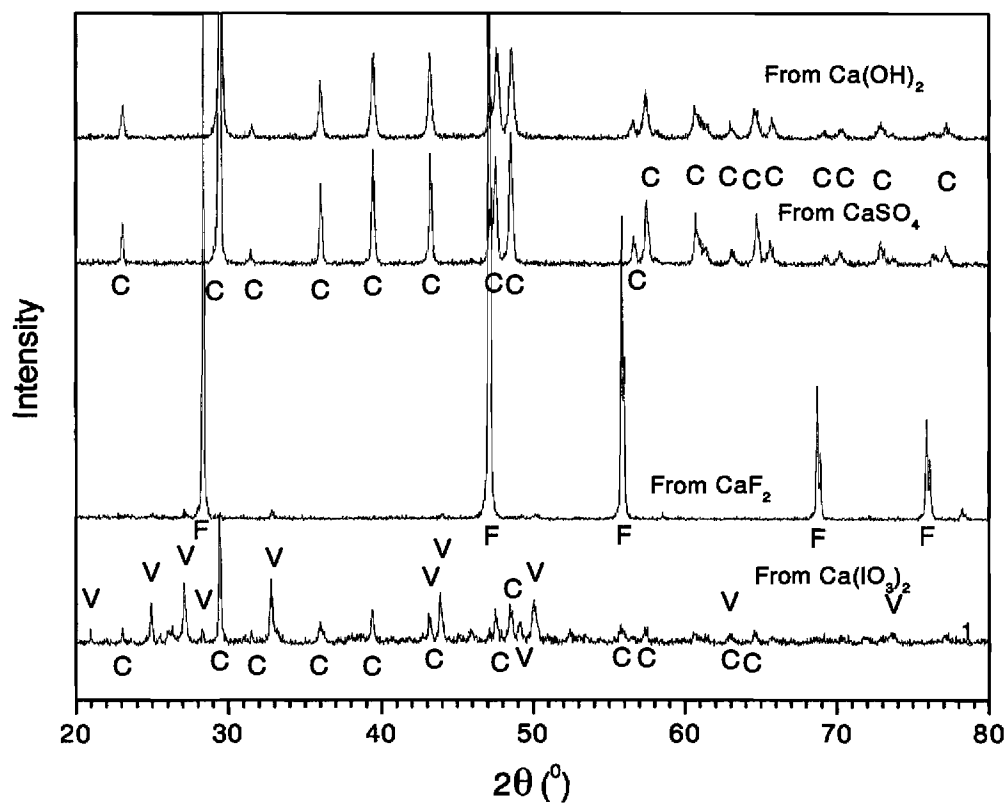


Fig. 1 Effect of reactants on crystal structure of PCC

Prepared from 50 mL 0.03 mol calcium salt suspension

and Na_2CO_3 aqueous solution at 70°C

C: Calcite CaCO_3 V: Vaterite CaCO_3 ; F: CaF_2

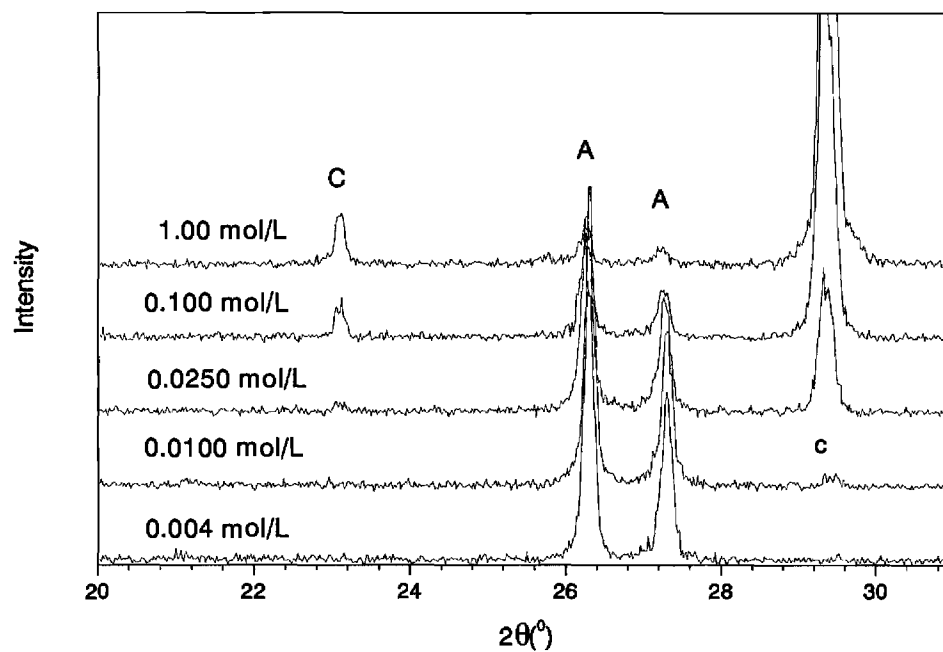


Fig. 2 Effect of Na_2CO_3 concentration on crystal structure of calcium carbonate

Prepared from 100 mL 0.03 mol of CaSO_4 suspension and

Na_2CO_3 aqueous solution at 70°C

A: Aragonite; C: Calcite

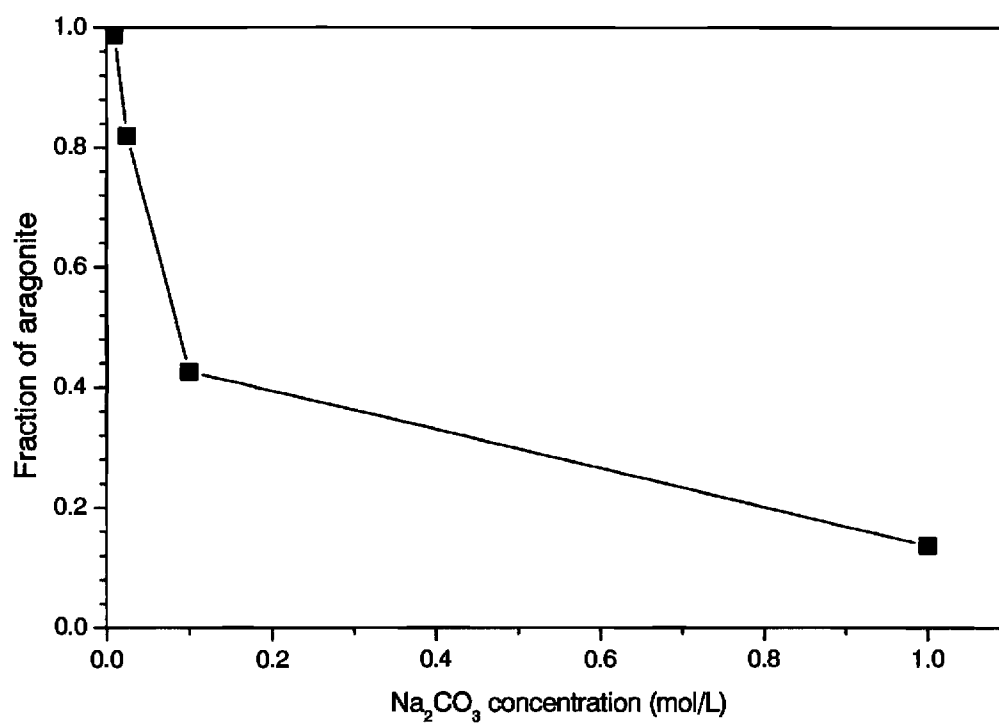


Fig. 3 Effect of Na_2CO_3 concentration on polymorphs of calcium carbonate

Prepared from 50 mL 0.03 mol of CaSO_4 suspension
and 1.00 mol/L Na_2CO_3 at 70°C with 0.64 mol/L Na_2SO_4

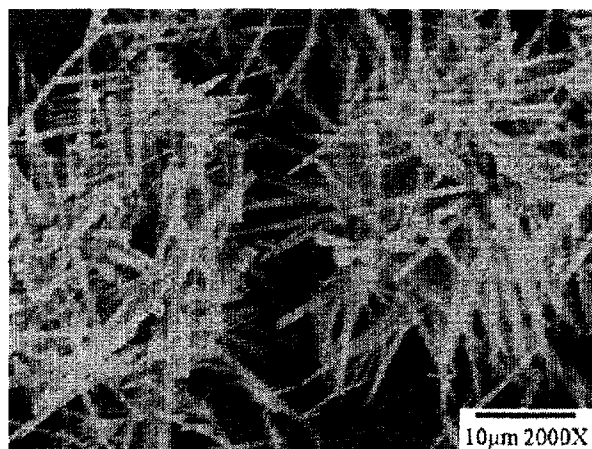


Fig. 4a from 0.004 mol/L Na_2CO_3

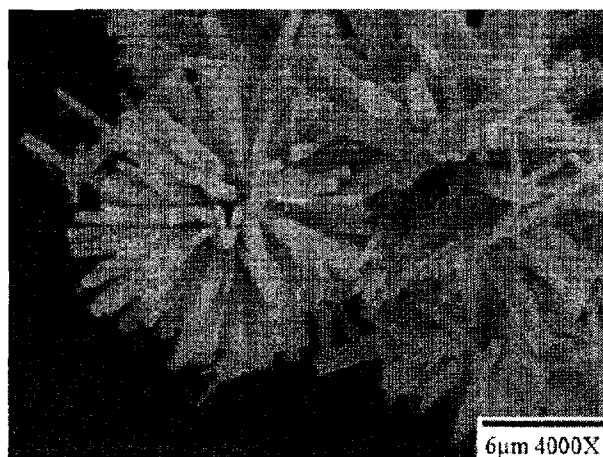


Fig. 4b from 0.01 mol/L Na_2CO_3

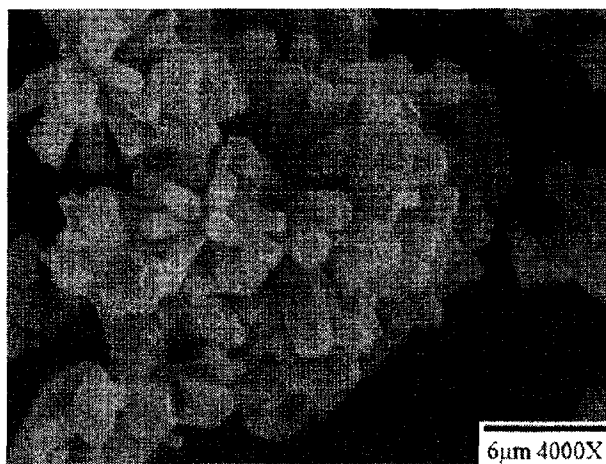


Fig. 4c from 0.025 mol/L Na_2CO_3

Fig. 4 SEM image of effect of calcium carbonate concentration

Prepared from 100 mL 0.03 mol of CaSO_4 suspension
and Na_2CO_3 aqueous solution at 70°C

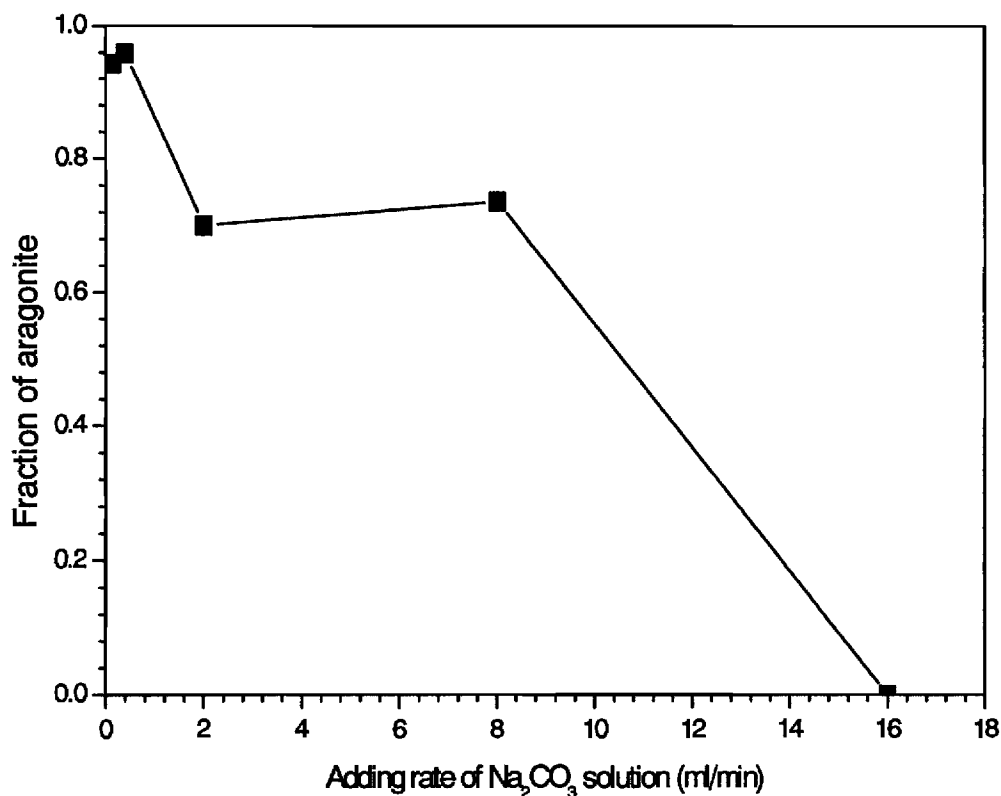


Fig. 5 Effect of adding rate of Na_2CO_3 concentration on polymorphs
of calcium carbonate

Prepared from 50 mL 0.03 mol of CaSO_4 suspension
and 1.00 mol/L Na_2CO_3 at 70°C with 0.64 mol/L Na_2SO_4

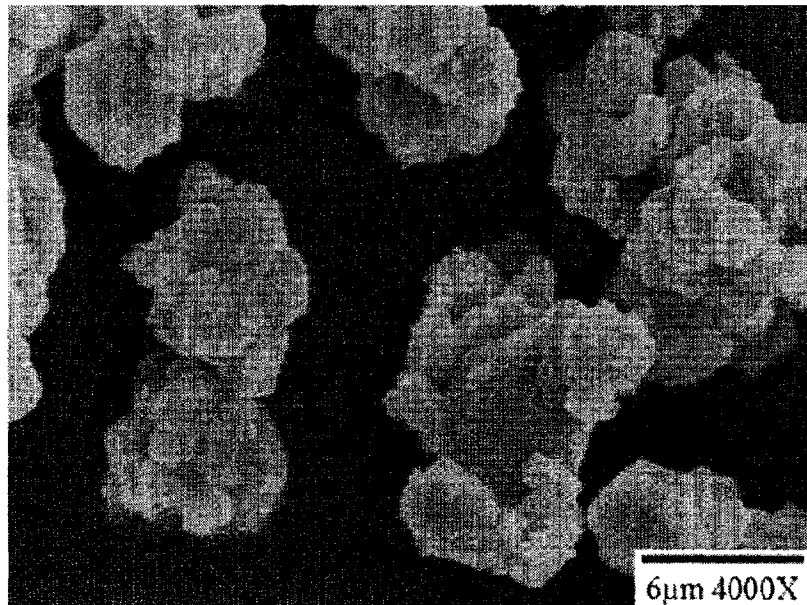


Fig. 6 SEM image of PCC prepared at a Na_2CO_3 adding rate of
0.15 mL/min

Prepared from 50 mL 0.03 mol of CaSO_4 suspension
and 1.00 mol/L Na_2CO_3 at 70°C with 0.64 mol/L Na_2SO_4

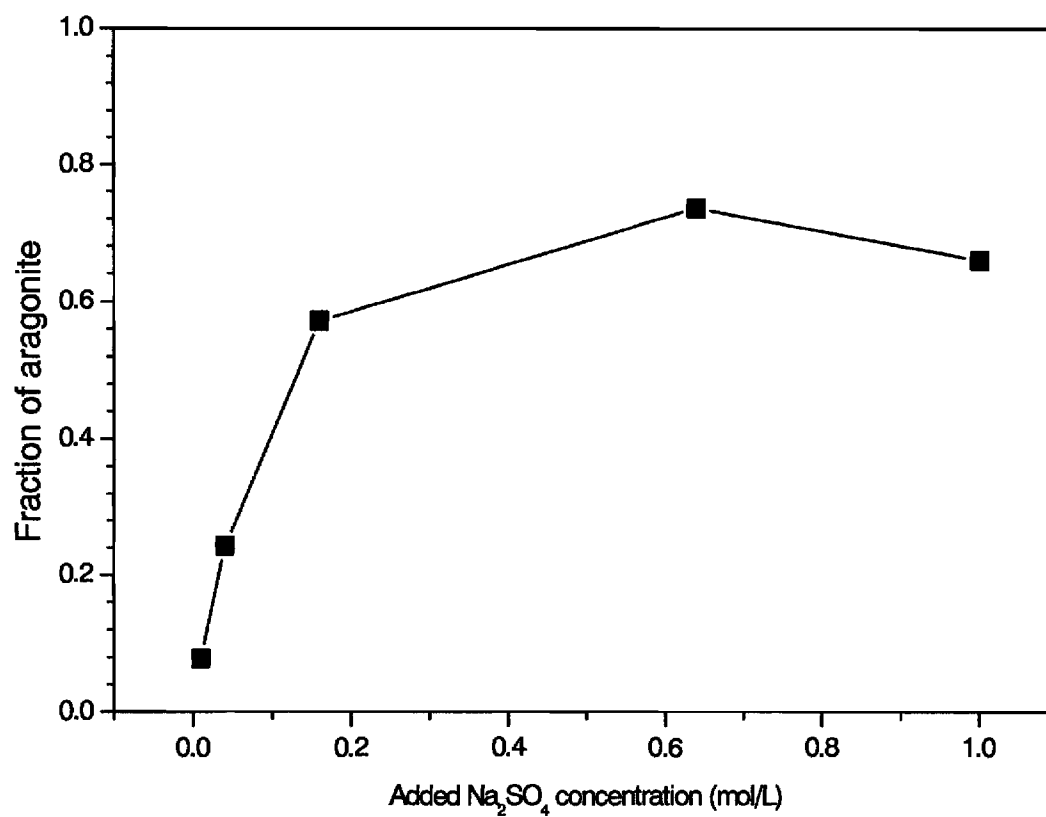


Fig. 7 Effect of added Na_2SO_4 concentration on polymorphs of calcium carbonate

Prepared from 50 mL 0.03 mol of CaSO_4 suspension

and Na_2CO_3 in aqueous solution at 70°C

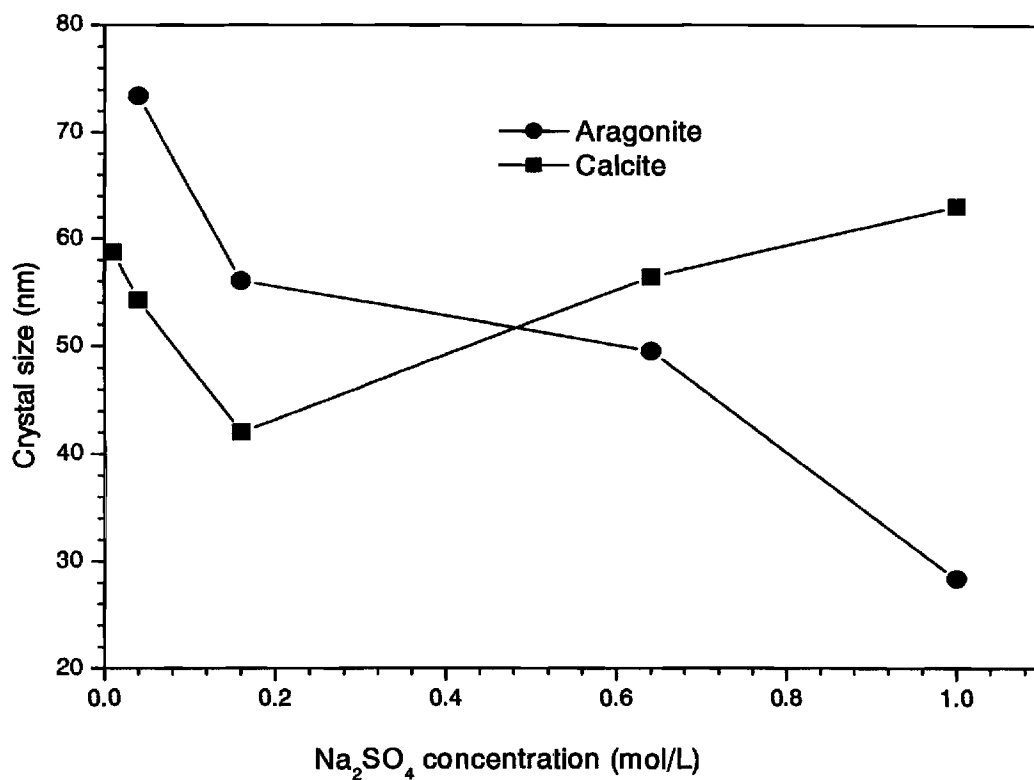


Fig. 8 Effect of added Na₂SO₄ on crystal size of calcium carbonate

Prepared from 50 mL 0.03 mol of CaSO₄ suspension

and Na₂CO₃ in aqueous solution at 70⁰C

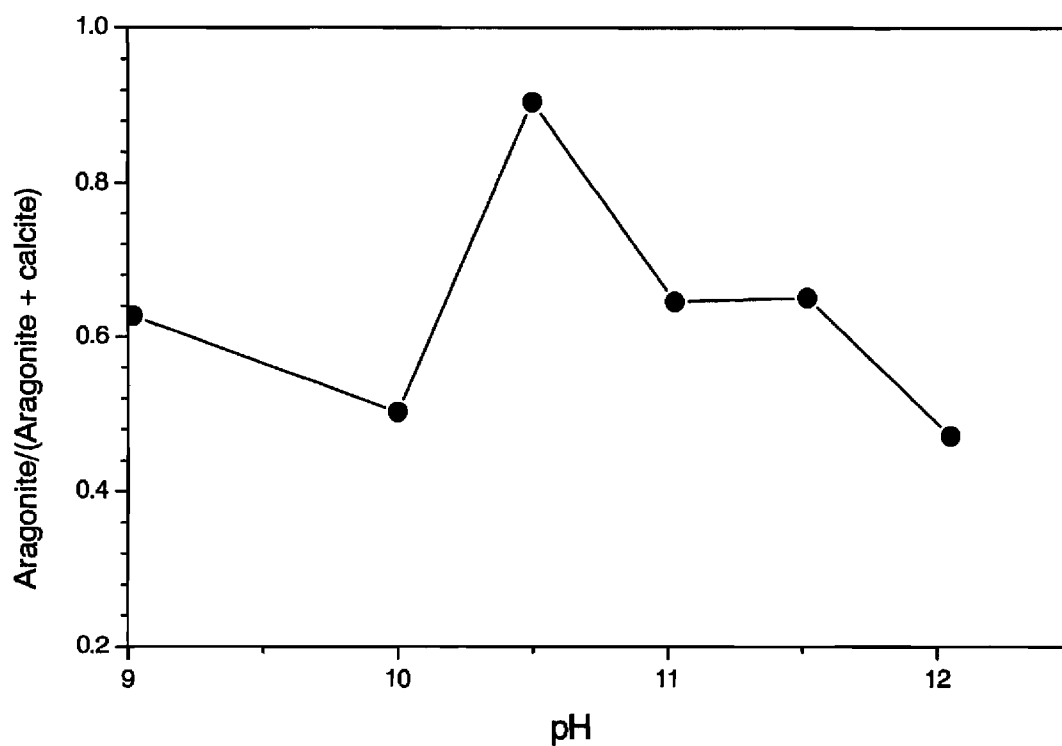


Fig. 9 Effect of pH of solution on polymorphs of calcium carbonate

Prepared from 50 mL 0.03 mol of CaSO_4 and Na_2CO_3 in aqueous solution

at 70°C . pH was adjusted with $(\text{NH}_4)_2\text{SO}_4\text{-NH}_3$

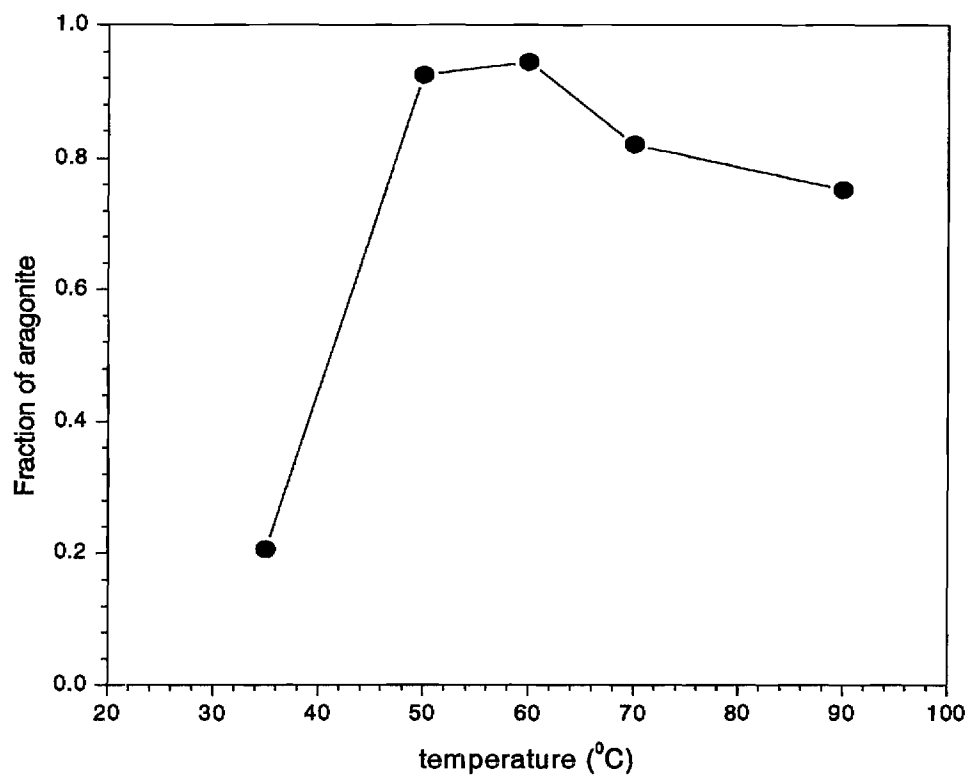


Fig. 10 Effect of temperature on polymorphs of calcium carbonate
Prepared from 50 mL 0.03 mol of CaSO_4 suspension
and 0.025 mol/L Na_2CO_3 in aqueous solution

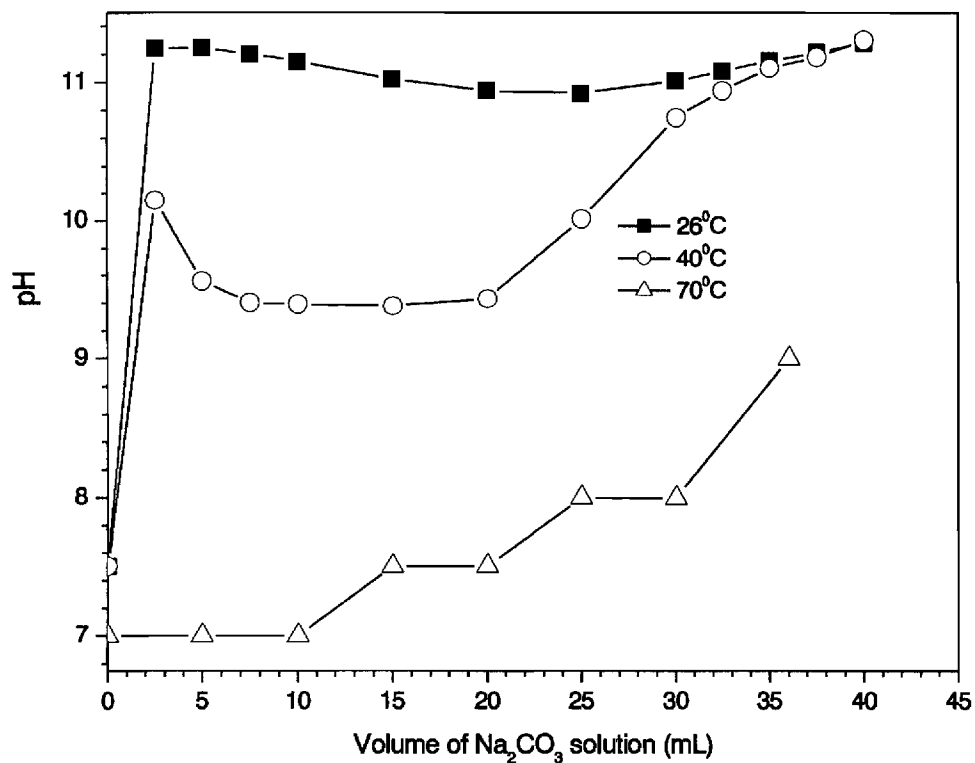


Fig. 11. Effect of temperature on pH of reaction solution

CaCO_3 prepared from 0.03 mol CaSO_4 in 50 mL of DI water with 0.04 mol/L Na_2SO_4
and 1.000 M Na_2CO_3 at an adding rate of 8 mL/min